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Urban influence on litterfall trace metals fluxes in the Atlantic forest of São Paulo (Brazil)

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Abstract. A monitoring project for two forest catchments was established in 2001 in São Paulo State, Brazil. The chosen catchments differed significantly with respect to human occupation. One catchment area, PEFI (23°39'S and 46o37'W), is inside the largest metropolis of South America, the city of São Paulo, within a Park of 549.3 ha, located about 50 km away from the ocean. The other catchment area, CUNHA (between parallels 23°13'18" and 23°16'10"South and meridians 45°02'53"and 45°02'53"West), is within a State Reserve of the Atlantic Forest, with 2850 ha, located about 15 km from the ocean, surrounded by rural areas and small villages. PEFI is about 798 m above sea level, while CUNHA is about 1050 m. In this work we examined the monthly litterfall trace metal (Fe, Mn, Zn, Cu, Cr, Pb, Cr, Cd, Hg) fluxes for both catchments during the 2001 dry season (may to September). Trace element concentrations were also determined in soils. CUNHA is characterized by low fluxes and low concentrations in soil, compared with PEFI. The same tendency was also observed for rainfall and throughfall Fe, Mn, Zn and Cu fluxes.

1. INTRODUCTION

The primary Brazilian Atlantic forest is one of the richest ecosystems in terms of biodiversity. It is also probably one of the most affected by industrial and automotive atmospheric emissions because the greatest urban and industrial centres of Brazil are located along the Atlantic coast. The deposition fluxes of trace metals on forest soils can originate from litterfall and throughfall. This latter corresponds to the rain water which penetrates the canopy and leaches the surface leaves. Because the canopy is an efficient trap for trace metal aerosols coming from polluted regions, this throughfall can be enriched in metals. The atmosphere is now recognized has being a key compartment in the transport of trace metals and, according to Forstner [1], in the case of soil contamination by Cd, Cu, Hg, Pb and Zn, the atmosphere can be one of the most important sources of these heavy metals. In order to understand the effects of these metals on the forest ecosystems, it is important to obtain information about the fluxes by which they are transported in the atmosphere/vegetation/soil system. In this system, the role of the litterfall in the trace metal deposition fluxes has also been pointed out by some authors [2,3]. This study aims to evaluate the influence of human atmospheric emissions on litterfall trace metal fluxes (Fe, Mn, Cu, Cr, Pb, Cd, Hg) in the Atlantic Forest, by comparing an area submitted to the influence of the São Paulo Metropolitan Region with an area located in a State Reserve of the Atlantic Forest.

II. MATERIALS AND METHODS

II.1. Study area

This study is part of a larger one, which aims to study the biogeochemical cycle and the transfer processes of chemical species in the interfaces of Atlantic forest ecosystem in two contrasting catchments. The

chosen catchments differed significantly with respect to human occupation. One catchment, PEFI (23°39'S and 46o37'W), is inside the largest metropolis of South America, the city of São Paulo, within a Park of 550 ha located about 50 km away from the ocean. The other catchment, CUNHA (between parallels 23°13'18" and 23°16'10"South and meridians 45°02'53"and 45°02'53"West), is within a State Reserve of the Atlantic Forest, with 2850 ha, and is about 15 km from the ocean, surrounded by rural area and small villages. This latter site was considered as a background region [4]. PEFI is about 798 m above sea level, while CUNHA is about 1050 m. For both catchments, the climate is wet tropical, characterized by rainy summers (November-April) and dry winters (May-October).

II.2. Sampling and chemical analyses

II.2.1. Litterfall

Four 1 m^2 litterfall traps were installed in each site, on each corner of a 30 x 30 m square. Traps were made of a 20 cm high wood frame with a nylon net bottom and stood about 20 cm above ground level. Although we are presenting here the results obtained for a dry period, May 2001 to October 2001, the litterfall was sampled monthly from May 2001 to April 2002. Samples were oven-dried at 60°C for a 24 h period; leaves and steams were sorted and weighted in order to evaluate the contribution of each to the litterfall composition. Only the leaves were ground and analyzed. Ground samples were wet digested with a mixture of concentrated HNO_3 and H_2O_2 in closed Teflon vessels in a microwave oven according to an adaptation of the method described by Rodushkin [5]. Fe, Mn, Zn and Cu concentrations were determined using inductively coupled plasma emission spectrometry (ICP-AES, Perkin Elmer-3000 DV) ; for Cr, Pb and Cd, the concentrations were determined by electrothermal atomic absorption spectrometry (ETAAS, Perkin Elmer-Aanalyst 400) ; Hg concentrations were determined by cold vapor atomic spectrometry (CVAAS, Buck Scientific-Mercury Analyser Vapor 400-A). Every sample was analyzed in duplicate and the analytical quality was checked by analysis of certified reference materials NIST 1515 (Apple Leaves) e NIST 1547 (Peach Leaves).

II.2.2. Soils

At the end of October 2001, twelve superficial (0-10 cm) soil samples were collected in each plot by using a plastic shovel. Wet sub-samples were digested according to the EPA 3050B method and metal concentrations (except Hg) were determined by ICP-AES. Hg concentrations were determined by CVAAS. In order to express the concentration results on a dry base, sample humidity was calculated after drying sub-samples at 110°C. Every sample was analyzed in duplicate and the analytical quality was checked by analysis of certified reference material CRM 2709 (San Joaquin Soil).

II.2.3. Fe, Mn, Cu and Zn atmospheric deposition

As already mention, this study is part of a larger one which aims to study the biogeochemical cycle and the transfer processes of chemical species in the interfaces of Atlantic forest ecosystem and from which it was possible to obtain data about atmospheric deposition [6]. Briefly, wet-only and bulk (i.e. wet + dry) deposition were collected weekly in an open area and througfall inside the florest within each catchment by using 167,45 cm^2 polyethylene plastic collectors. Each collector stood 1.5 m above ground level and had a collection area of 167,45 cm^2. Fe, Mn, Cu and Zn concentrations were determined by liquid ion chromatography, Dionex DX-500 with UV/Vis detector and CS5A column

III.RESULTS AND DISCUSSION

III.1. Litterfall deposition

Results of litterfall mass deposited during the study period are presented in Table 1. The statistical analysis (t-test, 95%) did not show any significant difference between the sites or between dry and rainy seasons.

Table 1. Litterfall fluxes deposited at CUNHA and PEFI areas during the study period (g/m^2)

	CUNHA	PEFI
Monthly means (05/2001 to 10/2001)	$66 \pm 47^{(a)}$	$61 \pm 44^{(a)}$
Total flux (05/2001 to 10/2001)	399	473
Total flux (05/2001 to 04/2002)	875	802

(a) : Mean ± standard deviation

III.2. Metal concentrations

Except for Mn and Cu, the metal concentrations in the litterfall were significantly ($p < 0.05$) higher at PEFI than at CUNHA (Table 2). On the other hand, in soils, higher concentrations were found at PEFI only for Cu, Pb, Cr and Hg. Higher metal concentrations in litterfall and soils could be due to a natural enrichment of some metals in PEFI soil. Nevertheless, Forti [6] showed that, for chemical species such as Ca^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, Fe, Cu, Zn and Mn, whose atmospheric concentrations are strongly influenced by human activity, the wet deposition was higher at PEFI than at CUNHA.

Table 2. Mean concentration (± standard deviation) of metals in litterfall and soil samples collected at CUNHA and PEFI (May to October 2001)

	LITTERFALL			**SOIL**		
	CUNHA	PEFI	Units	CUNHA	PEFI	Units
Fe	72 ± 48	244 ± 79	µg/g	17 ± 6	14 ± 3	mg/g
Mn	384 ± 110	505 ± 267	µg/g	55 ± 37	31 ± 11	µg/g
Zn	22 ± 6	39 ± 7	µg/g	22 ± 21	22 ± 21	µg/g
Cu	9 ± 1	9 ± 2	µg/g	6 ± 2	19 ± 2	µg/g
Pb	1.5 ± 0.5	6 ± 2	µg/g	11 ± 3	28 ± 3	µg/g
Cd	0.04 ± 0.01	0.6 ± 0.2	µg/g	< 0.6 (DL)	< 0.6	µg/g
Cr	0.1 ± 0.1	0.5 ± 0.1	µg/g	12 ± 3	18 ± 3	µg/g
Hg	72 ± 13	100 ± 20	ng/g	87 ± 15	116 ± 22	ng/g

DL : Detection limit

III.3. Trace metal fluxes

Except for Cu, the litterfall trace metal fluxes were always higher at PEFI than at CUNHA (Table 3), nevertheless the difference was significant only for Pb, Cr and Cd. Our values were similar to those reported by Mayer [7] who calculated the monthly litterfall fluxes for Fe, Mn, Cu and Zn in an Atlantic forest area of the Serra do Mar, also located in the São Paulo state but under the influence of the Cubatão industrial complex.

Table 3. Litterfall trace metals fluxes for the 6 month period (May to October, 2001) at CUNHA and PEFI.

	CUNHA	PEFI	Units
Fe	32	56,5	mg/m^2
Mn	163	241	mg/m^2
Zn	9	15	mg/m^2
Cu	3.3	2.1	mg/m^2
Pb	575	2297	$\mu g/m^2$
Cd	19	245	$\mu g/m^2$
Cr	67	181	$\mu g/m^2$
Hg	30	34	$\mu g/m^2$

For Fe, Mn, Zn and Cu, atmospheric and throughfall fluxes were calculated based on the data communicated by Forti [6]. At CUNHA no difference was observed between bulk and wetonly fluxes, indicating that in this area it does not exist any significant dry deposition. At PEFI, the dry deposition was mainly significant for Zn and Mn, pointing out the influence of the human activity from the São Paulo metropolitan region on the atmospheric deposition at the PEFI area.

IV. CONCLUSION

Ours results showed that, at least during the dry season, trace metal concentrations are generally higher in the soil and the litterfall at PEFI than at CUNHA. For Pb, Cr and Cd deposition fluxes via litterfall were also significantly higher at PEFI. These differences can be attributed to the influence of the human activity from the Saõ Paulo metropolis, which increases the atmospheric concentrations of some trace metals and consequently their deposition fluxes on the near forest ecosystem. In spite of the increase of trace metal concentrations at PEFI, it was verified that concentrations in soil and litterfall are still law, being in the same range of background levels [8,9]. Soon, ours results will be completed, allowing to estimate trace metal input-output budgets in order to better understand the role of the litterfall in the trace metal deposition fluxes on forest soils.

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